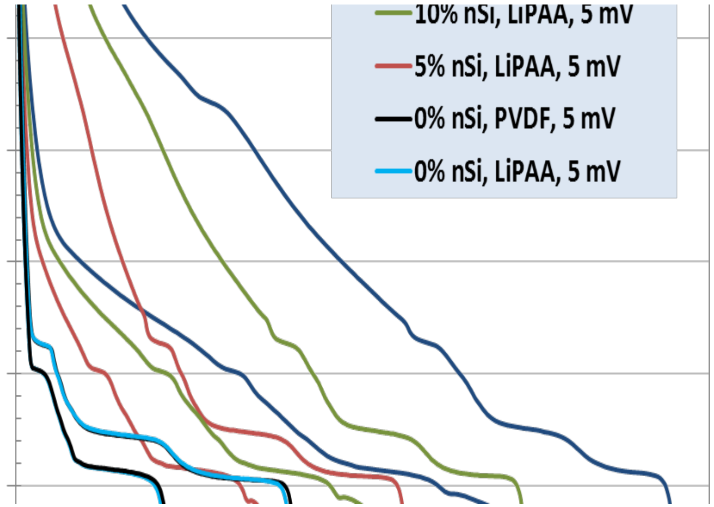
NEXT GENERATION ANODES FOR LITHIUM-ION BATTERIES: OVERVIEW

Silicon Deep Dive



DENNIS DEES

2017 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING

Project ID ES261

OVERVIEW

Timeline

- Start: October 1, 2015
  - Reset: October 1, 2016
- End: September 30, 2019
- Percent Complete: 40%

Budget

- Total project funding:
  - FY17 - $3600K
- ES261 and ES335

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety

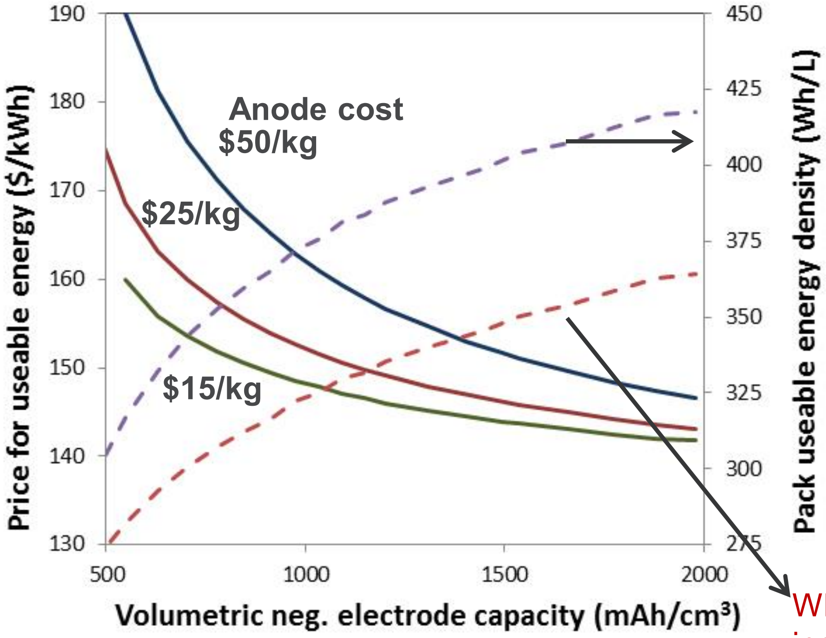
Partners

- Sandia National Laboratories
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

RELEVANCE

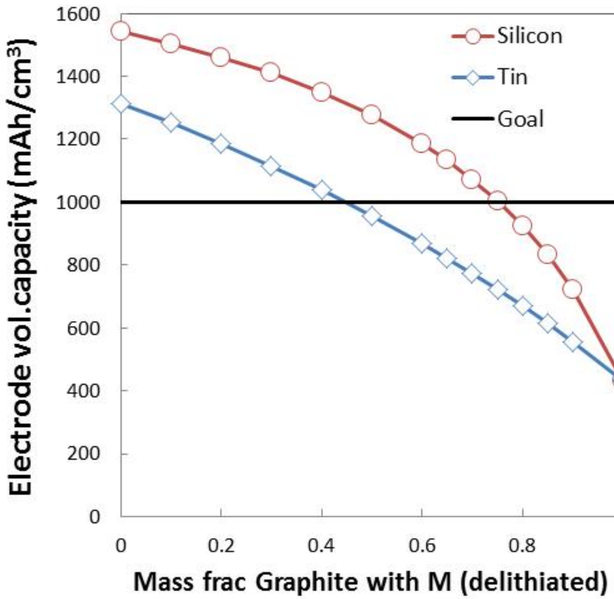
Battery Performance and Cost (BatPaC) Model Utilized to Establish Relevance by Connecting Pack to Anode Targets

- Pack level benefits reach diminishing returns after **1000 mAh/cm³** for both cost and energy density
  - mAh/cm^3 [electrode basis] = $\rho \cdot \varepsilon \cdot Q$ [$g/cm^3_{act} \cdot cm^3_{act}/cm^3_{elect} \cdot mAh/g$]
- Silicon with <75 wt% graphite can achieve target



Wh/L including foam between cells 2x volume expansion

45 kWh_{use}, 90 kW 360 V
$20/kg 200 mAh/g NMC cathode



Electrode volumetric capacity uses lithiated basis $Li_{4.4}Si$ or $Li_{4.4}Sn$ and maximum active material volume fraction of 65%

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APPROACH

- **Objectives: Stabilize the SEI - Stabilize the Electrode**
- **Overall Focus on Insights into and Advancement of Silicon-Based Materials, Electrodes, and Cells (SiBMECs).**
- **Developments will be Incorporated into Baseline SiBMECs.**

- Anode advancements verified based on life and performance of full cells.
  - Utilize established baseline SiBMECs and testing protocols.
  - Supported by Cell Analysis, Modeling, and Prototyping (CAMP) facility and Battery Manufacturing Facility (BMF)
- Plan and conduct a wide range of electrochemical and analytical diagnostic studies on SiBMECs.
  - Establish structure-composition-property relationships.
  - Lithium-alloying surface and bulk transport and kinetic phenomena.
  - Assessment of failure modes.
  - Supported by Post-Test Facility (PTF)
- Evaluation of safety and abuse tolerance of SiBMECs.
  - Supported by Battery Abuse Testing Laboratory (BATLab)

APPROACH (CONTINUED)

- **Objectives: Stabilize the SEI - Stabilize the Electrode**
- **Overall Focus on Insights into and Advancement of SiBMECs.**
- **Developments will be Incorporated into Baseline SiBMECs.**

- Materials development on SiBMECs to enhance interfacial stability, accommodate intermetallic volume changes, and improve overall performance and life.
  - Explore lithium inventory strategies.
  - Study alternative high-energy metals: $Me_xSi_{0.66}Sn_{0.34}$ (Me: Cu, Ni, Fe, Mn).
  - Examine a wide range of functional binders.
  - Interfacial modifications: MLD/ALD, surface coatings, and electrolyte additives.
- Materials advances can be scaled-up with the support of the Materials Engineering Research Facility (MERF).
- Materials advances will be incorporated into baseline SiBMECs with support of BMF and CAMP facility.
- Communicate progress to battery community.
  - Open to industrial participation and/or collaboration that does not limit program innovation or the free flow of information.

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FY17 CHANGES IN SILICON DEEP DIVE PROGRAM

Silicon Deep Dive Program

- Electrochemical and Analytical Diagnostics
- Facility Support
- Interfacial Modifications
- Polymer Binders
- Active Materials Development
- Model Systems Studies

Focus on Electrode and Full Cell Studies

Strong Program Communication and Support

Silicon Electrolyte Interface Stabilization (SEI-Sta) Focus Group ES333

Focus on Model Systems and SEI Stability Studies

MILESTONES AND ACTIVITIES

- **The program has more than twenty-five milestones related to the broad range of interactive activities listed below.**
- **Generally, milestones are either completed or on schedule except for aqueous-based silicon electrode process development, whose challenges are described in more detail in the technical section.**

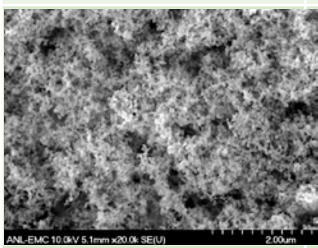
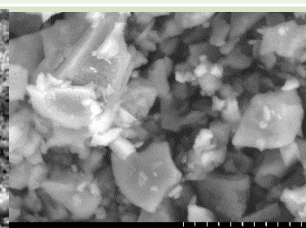
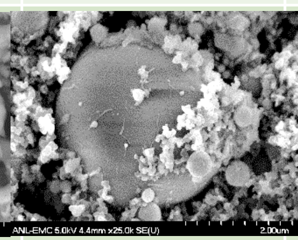
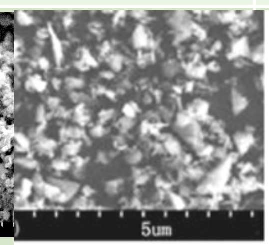
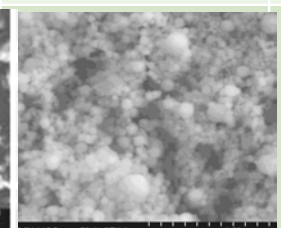
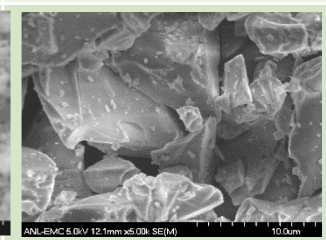
- Extensive electrochemical and analytical diagnostic studies.
- Facilities supporting program through a wide range of studies.
  - Battery Abuse Testing Laboratory (BATLab); Battery Manufacturing Facility (BMF); Cell Analysis, Modeling, and Prototyping (CAMP); Materials Engineering Research Facility (MERF); Post-Test Facility (PTF)
- Development and testing of coatings and additives designed to modify and stabilize the interface.
- Develop and analyze polymer binders designed to accommodate volume changes, increase conductivity, and improve adherence.
- Active material development.
  - Explore lithium inventory strategies.
  - Study alternative high-energy metals.

For reviewers, a detailed list of the milestones and progress is supplied in the reviewers only slides.

SEARCH FOR NEW SILICON POWDER BASELINE

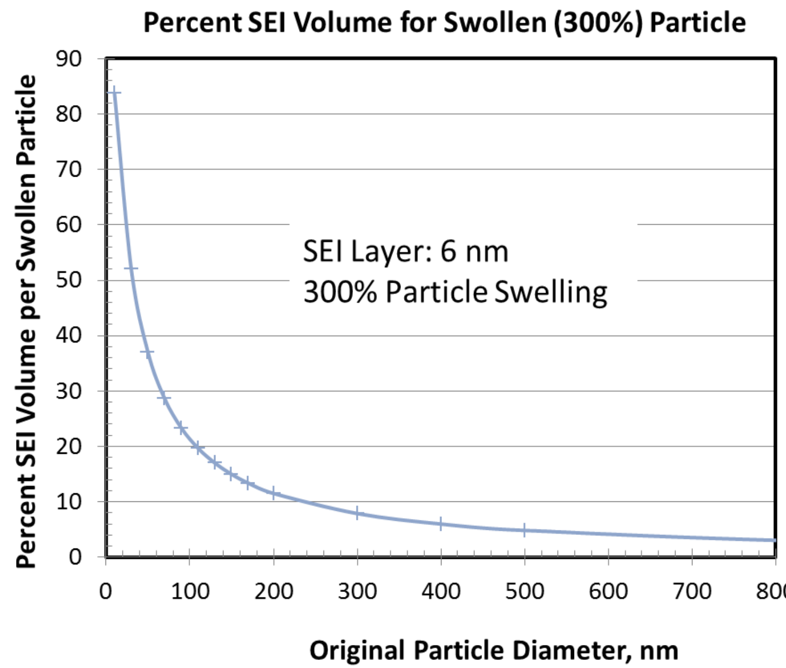
- 50-70 nm silicon from NanoAmor (original baseline) discontinued
- Search was conducted for commercially available silicon materials that could be used openly in the Next Generation Anodes Project (Si Deep-Dive)
- A variety of Si materials were obtained and characterized using NMR, SEM, and electrochemical testing
  - Considerable differences in morphology were seen based of method of production: grown versus milled

Also See ES030

NanoAmor	NanoAmor	American Elements	American Elements	Hydro-Quebec	Aldrich
30-50 nm Si	70-130 nm Si	150 nm Si	500 nm Si	80 nm Si	40 μm SiO
Grown	Milled	Grown	Milled	Grown	Grown/milled
					

OPTIMUM SILICON PARTICLE SIZE

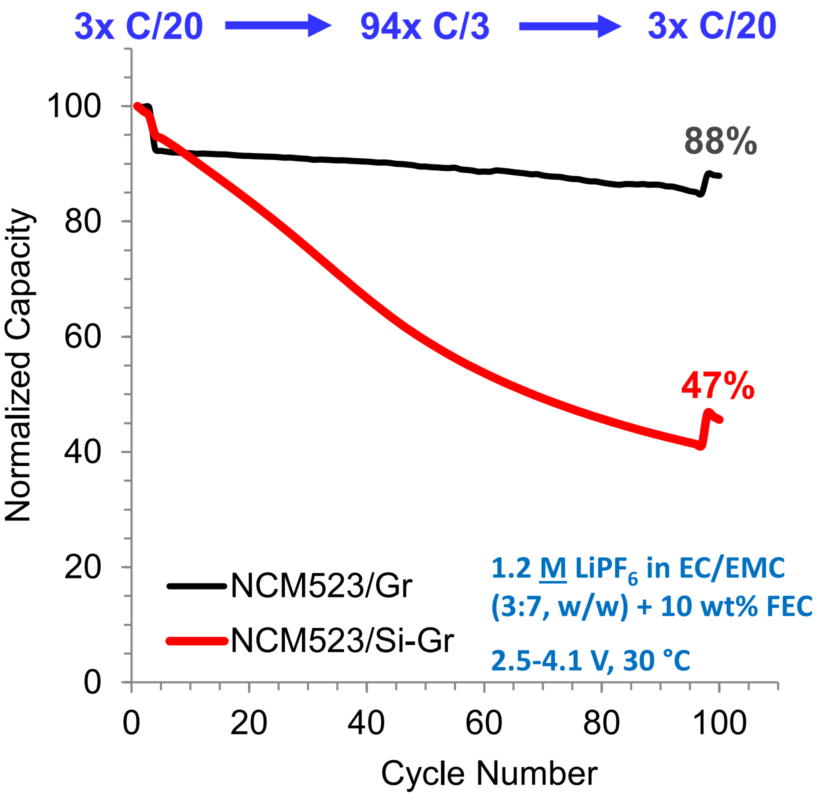
- Literature indicates that silicon particles less than 200 nm are needed to minimize impact of fracturing during cycling.
- However, smaller silicon particles lead to excessive SEI formation and reactivity.
  – SEI thickness measured by FTIR & XPS indicated that SEI volume severely impacts energy density for small Si.
  – Calorimetry studies indicate excessive heat during thermal runaway for 15% Si anodes (50-70 nm) vs. NMC532 at 100% SOC in 1.2 Ah 18650 cells.

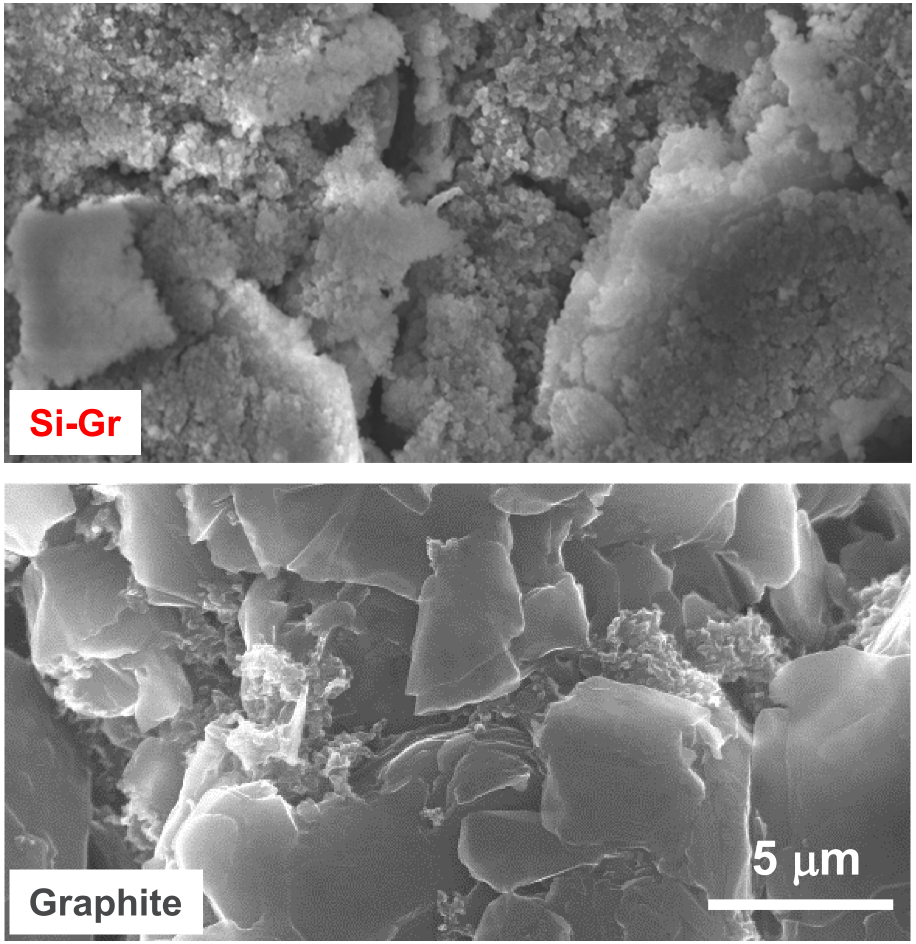


- Decided to move to larger particle size, such as NanoAmor 70-130 nm Si.
  – However, after numerous electrode variations, this material did not coat or perform as well as the 50-70 nm Si at high loadings (~3.5 mAh/cm²).
- Search for improved baseline silicon powders continuing.
  – Initial results with open-source Si from Paraclete Energy promising.

SEM IMAGES SHOW MUCH MORE SEI ON SI-GR THAN ON GRAPHITE (GR) ELECTRODES

SiGr or Gr electrodes harvested from Full Cells after 100 cycles





Si-Gr cells display poorer capacity retention (more Li^+ ions lost to SEI)

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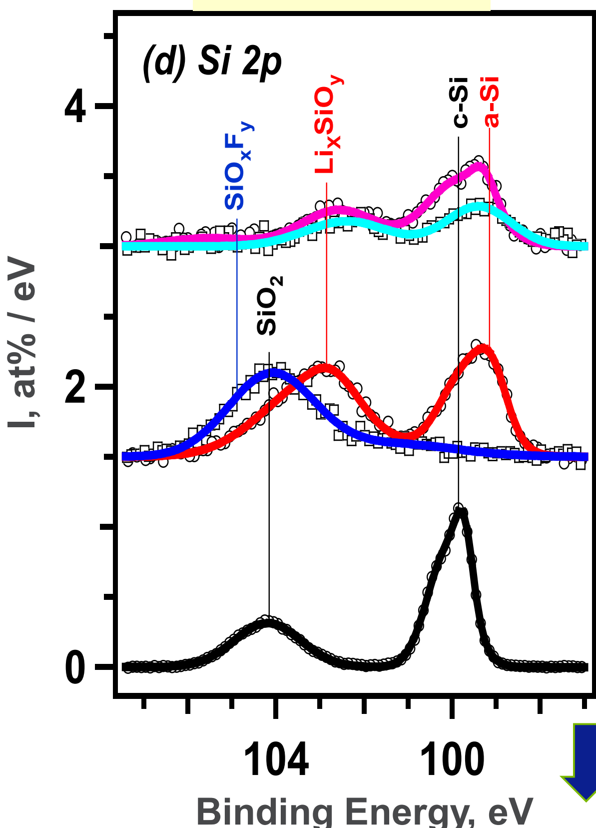
XPS DATA SHOWS SI AT POSITIVE FOR NMC532/SI-GR CELLS WITH GEN2 ELECTROLYTE

Positive Electrodes from FEC-additive cells do not show Si

Si-Gr Negative

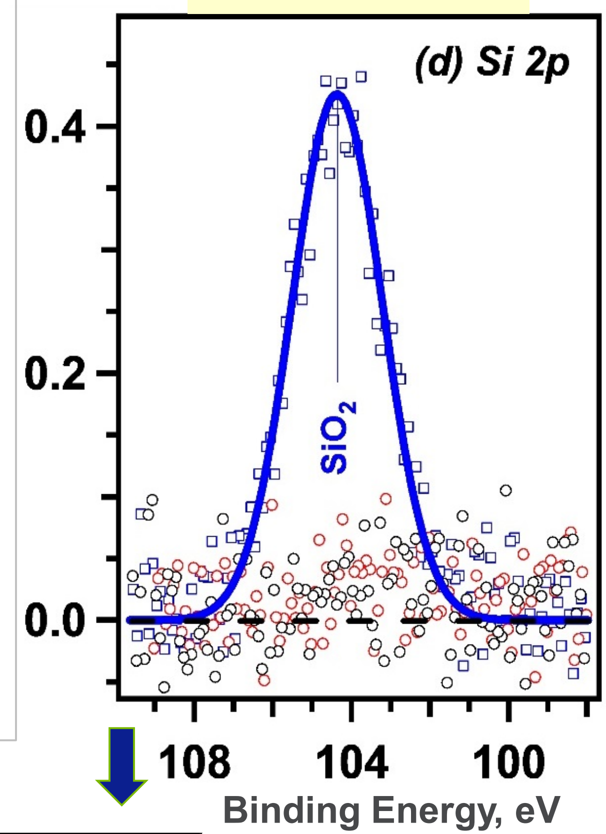


XPS and NMR data show

- SiO_xF_y signals at the Si-Gr electrode
- $Li_xPO_yF_z$ compounds in the electrolyte
- SiO_2 species on positive electrode
- $LiPF_6$ hydrolysis products in electrolyte

Residual moisture from electrode fabrication process could generate HF that accelerates performance loss

NMC532 Positive



Color Code

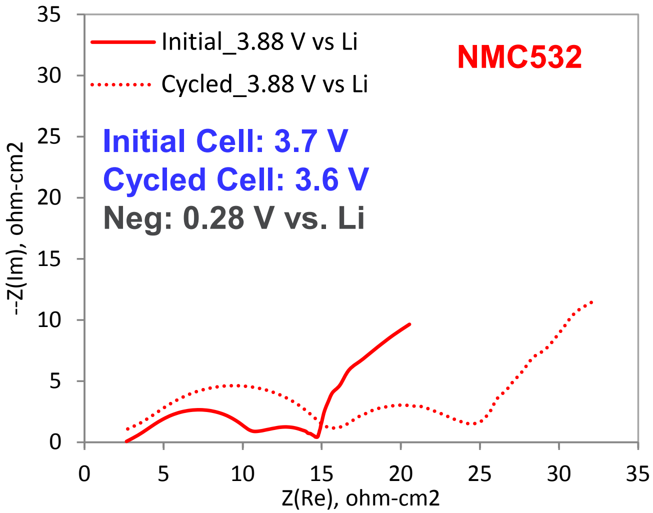
# Cycles	0	3	100	3	100
Electrolyte	Pristine	Gen2	Gen2	+10% FEC	+10% FEC

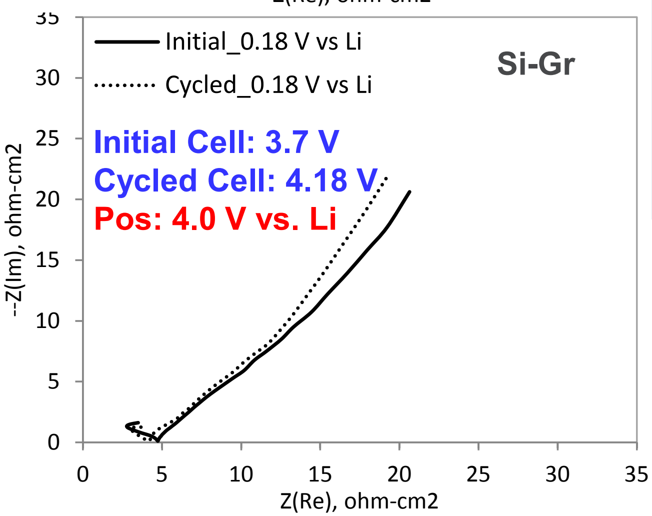
Gen2 Electrolyte

1.2 M $LiPF_6$ in EC/EMC (3:7)

ELECTRODE IMPEDANCE CHANGES – EFFECT OF CYCLING ON A NMC532/SI-GR CELL W/FEC

Data with Li_xSn Reference electrode. EIS: 100kHz – 0.005 Hz, 30°C





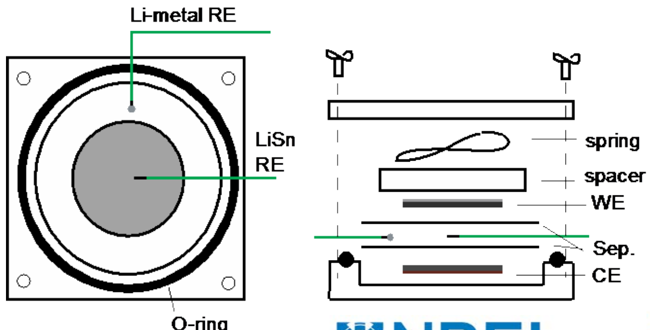
Impedance rise on cycling is mainly at the positive electrode

Electrode potential windows shift occur on aging because of Li^+ ion trapping at the negative electrode.

When electrode potentials of the cycled cell are matched to the initial values we note the following:

Impedance increases in the high- and mid-frequency arcs arise from the positive electrode.

Impedance changes at the negative electrode are small.



External Li metal RE
For tracking electrode potentials during cycling
Internal 25 micron Li_xSn RE
Used for DC and AC impedance measurements

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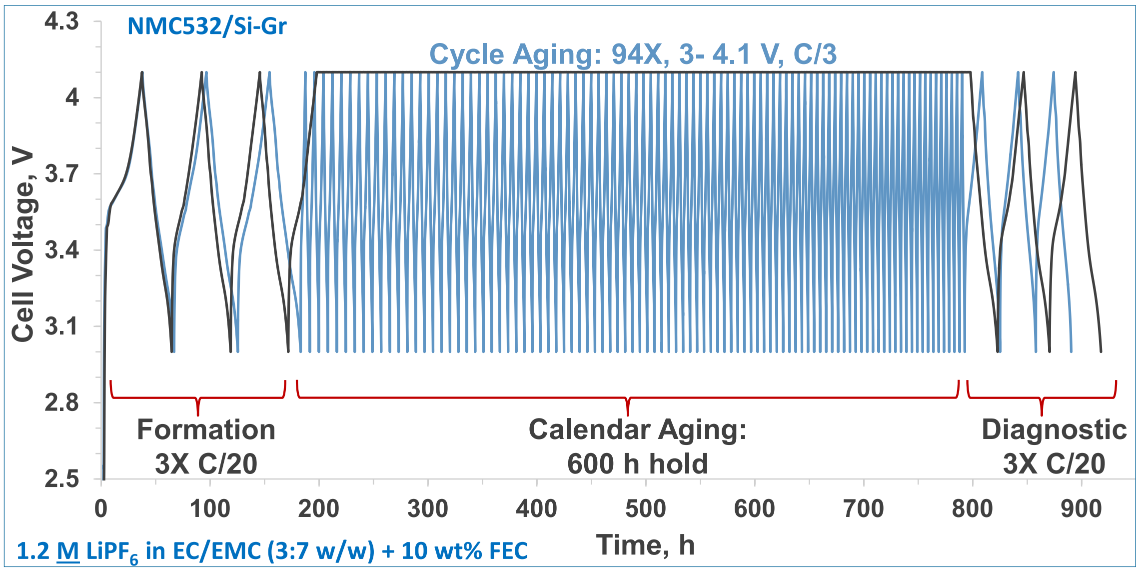
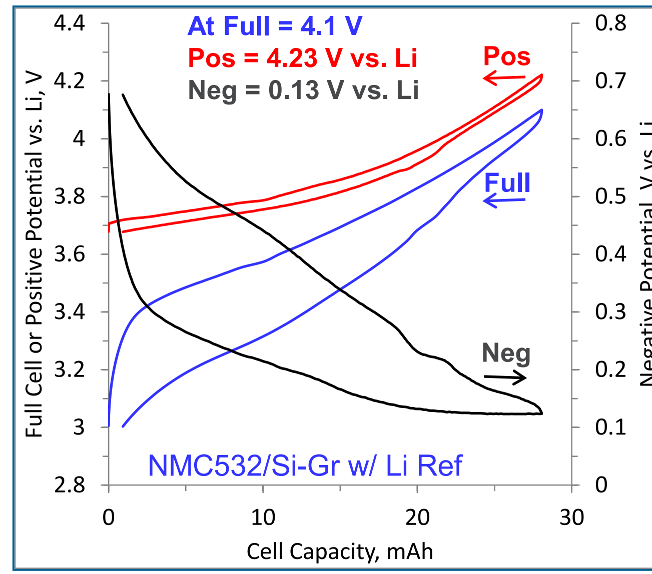
CALENDAR LIFE AGING STUDIES SHOW THAT SI-GR ELECTRODES DO NOT FULLY PASSIVATE

Capacity loss is lower for calendar-life than for cycle-life aged cells



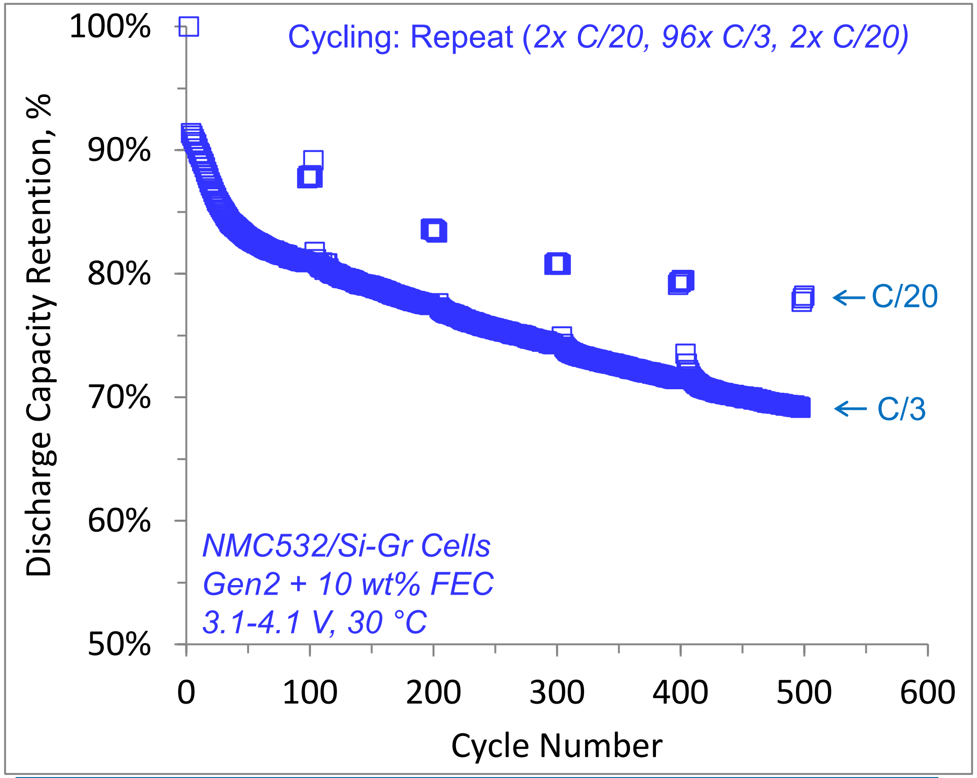


Volume changes in Si (and Gr) particles during cycle aging can fracture SEI and enhance Li^+ ion loss. These volume changes should be minimal during calendar aging as the Si-Gr electrode potential is relatively stable (~0.13 V vs. Li, in this test). *A truly-passivating SEI should thus result in 0% capacity fade*. **In our experiment, the 3-4.1 V cycled cell showed 46% capacity loss, while the 4.1 V calendar cell showed 11% capacity loss**. This 11% loss indicates parasitic side-reactions even in the absence of volume changes.

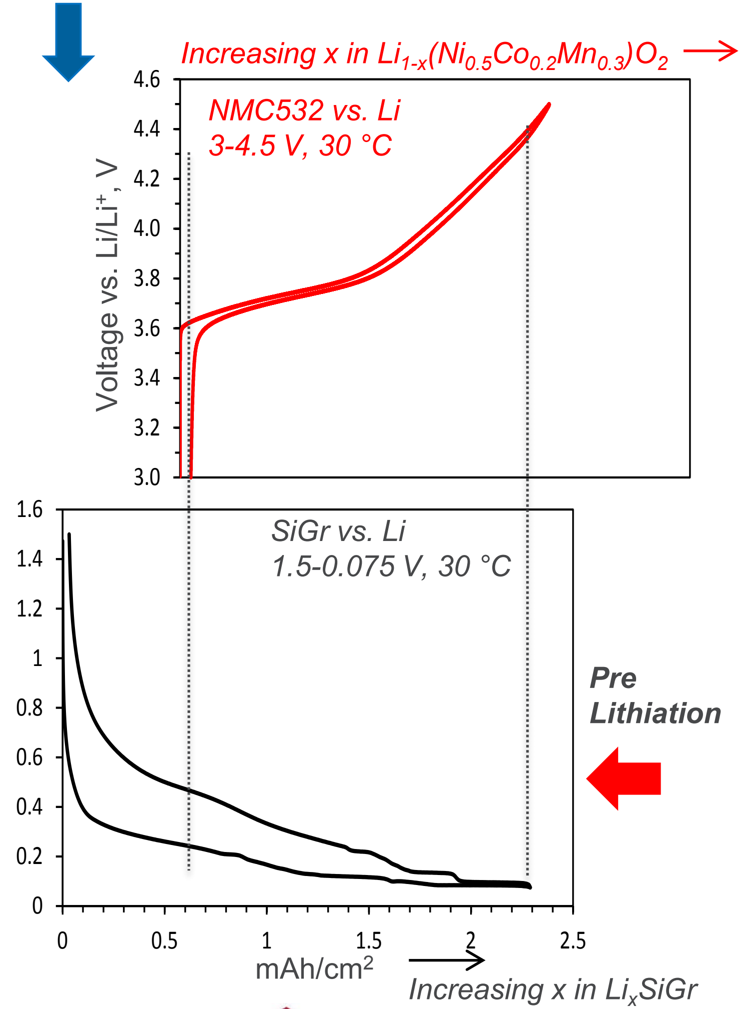
Also See ES030

FULL CELLS WITH PRELITHIATED SI-GR ELECTRODES SHOW GOOD PERFORMANCE

Prelithiation alters electrode cycling windows



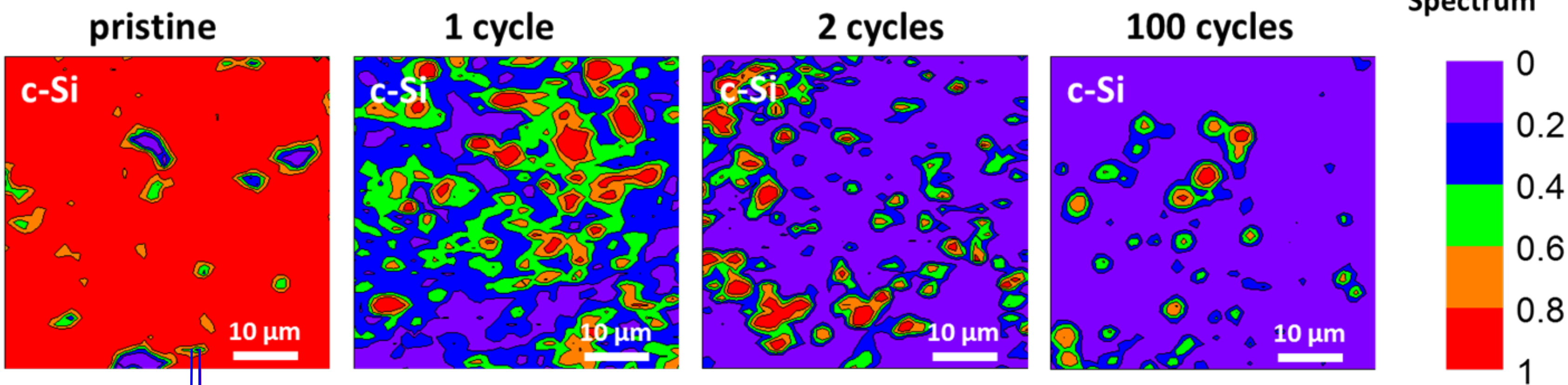
Prelithiating Si-Gr prolongs cell life
88% capacity retention after 100 cycles (C/20)
78% capacity retention after 500 cycles (C/20)

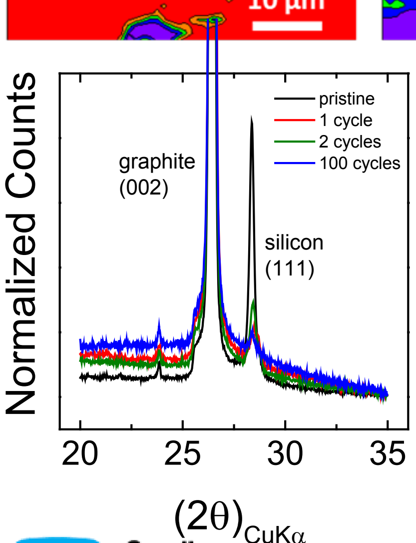


RAMAN MAPPING SHOWS SOME SILICON IS ELECTROCHEMICALLY INACTIVE

Pristine and cycled anodes harvested from NMC532 / Si-Graphite full pouch cells

Maps of the relative contribution of c-Si to the Raman spectra



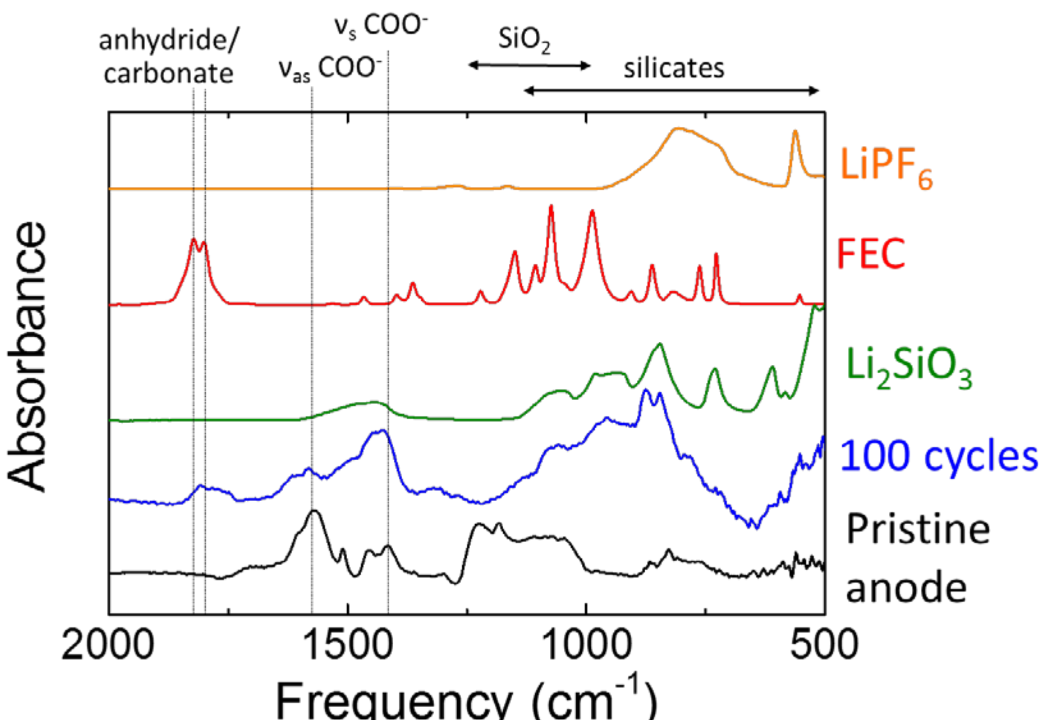


- Raman micro-spectroscopy was used to map the relative concentrations of c-Si, a-Si, and graphite in Si anodes before and after cycling.
- Most c-Si transforms to a-Si after the first cycle, but some c-Si remains after 1, 2, and 100 cycles.
- XRD confirms that some silicon is electrochemically inactive and remains crystalline.

FTIR SHOWS SIGNIFICANT CHANGES IN LiPAA BINDER AFTER CYCLING

Pristine and cycled anodes harvested from NMC 532 / Si-Graphite full pouch cells

- Shift in carboxylate stretches (~1570 and 1410 cm^{-1}) compared to pure LiPAA show binder interacts with SiO_2 surface.
- Relative intensities of symmetric and asymmetric carboxylate stretches change after 100 cycles.



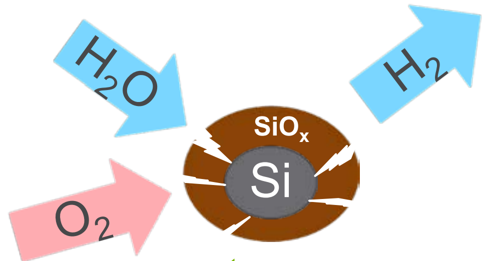
Lithium silicates form by reaction of SiO_2.

The formation of other common SEI components cannot be ruled out:

- alkyl carbonate salts
- carboxylate salts
- Li_2CO_3
- P- and F-containing species

HYDROGEN GASSING DURING AQUEOUS-BASED SILICON ELECTRODE PROCESSING

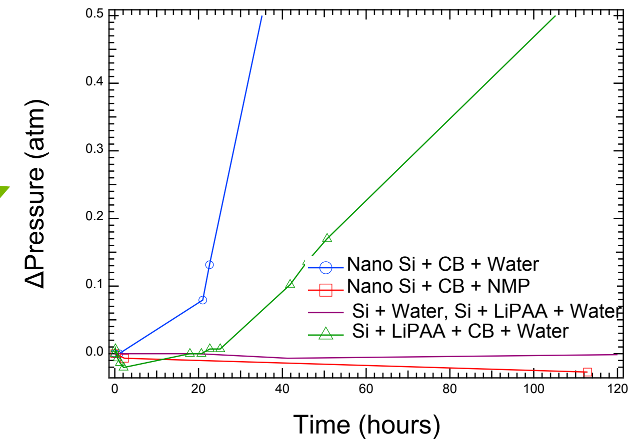
- Additional mixing needed via planetary ball mill to minimize Si agglomeration and improve carbon black dispersion
- Nanoamor Si (70-130nm) reacts with H_2O to produce H_2 and additional SiO_x
- Si reacted to form SiO_x and passivates in NMP through O_2 consumption



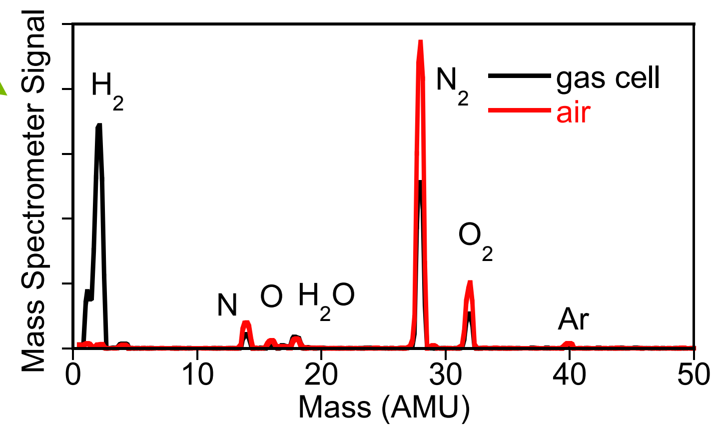
$$Si + H_2O \rightarrow SiO_x + H_2$$

$$Si + O_2 \rightarrow SiO_x$$

Pressure monitoring during slurry mixing



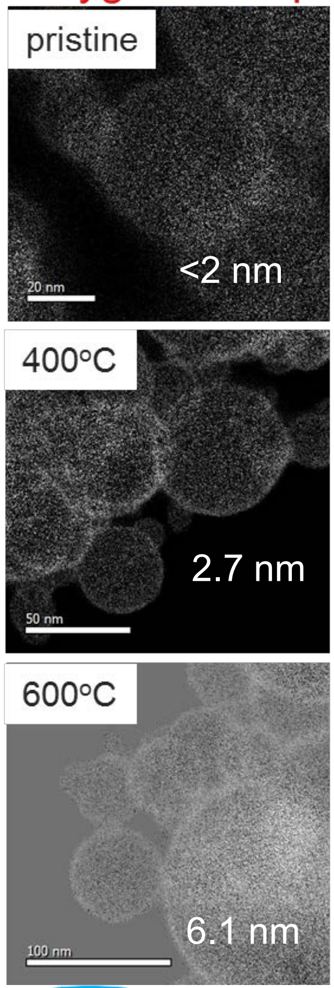
Mass spectroscopy of gas from slurry



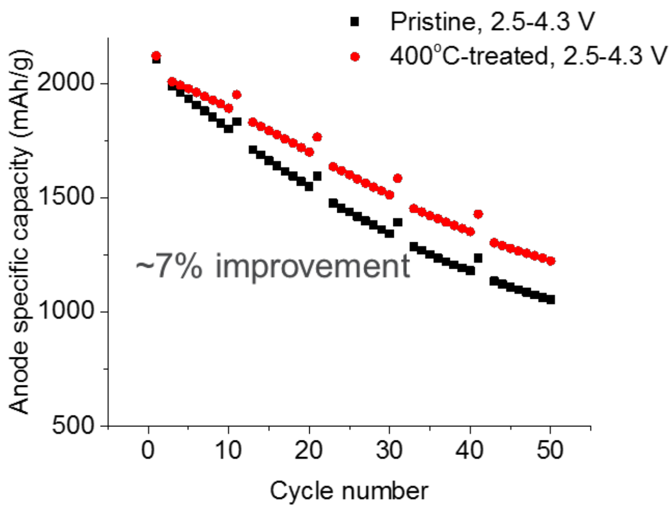
HEAT TREATING Si TO ADJUST THE OXIDE LAYER FOR OPTIMAL PERFORMANCE AND PROCESSING

Si nanoparticles with ~80 nm diameter were oxidized at 300-700℃.

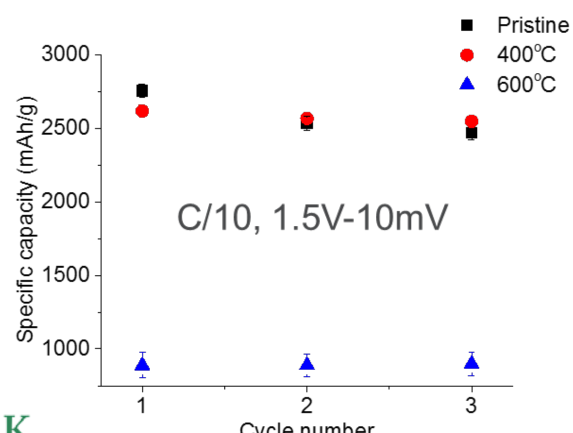
Oxygen K map



Si/NCM523 Full Cell cycling



Li/Si Half Cell Formation



Original pouches

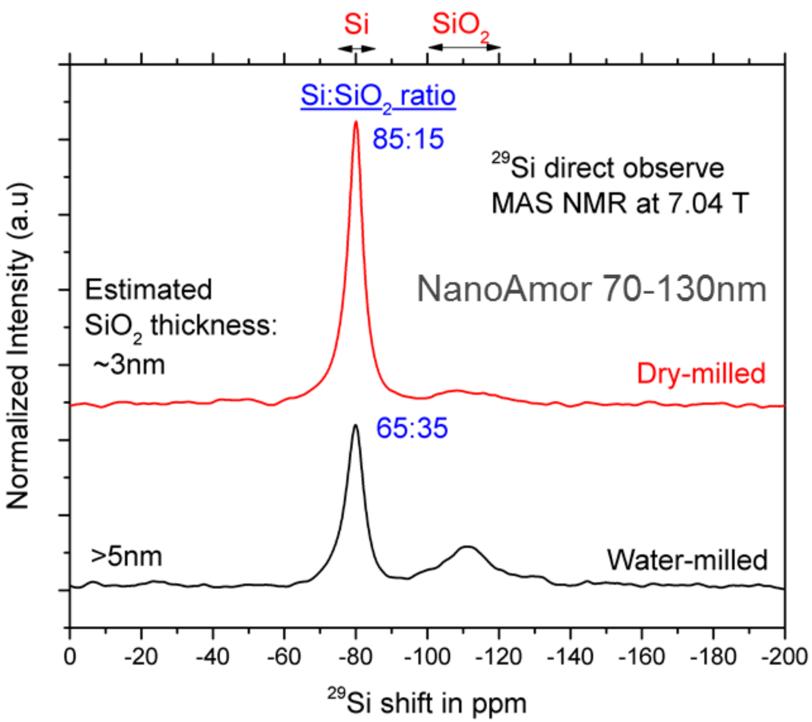
3 days, 75℃

Slurry consists of silicon, carbon black, and LiPAA aqueous solution.

NMR SPECTROSCOPY USED TO STUDY SILICON, MATERIAL INTERACTIONS, AND ELECTRODES

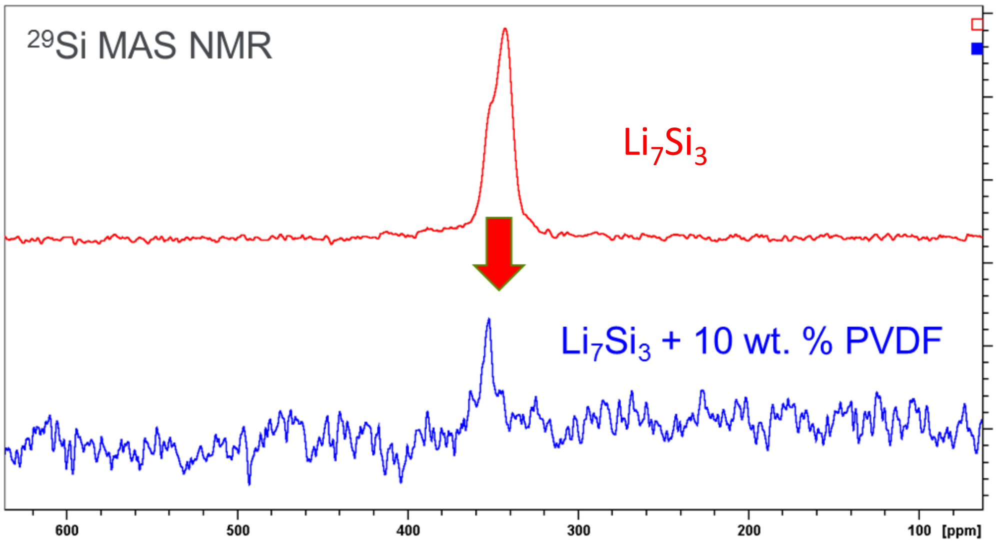
- ***ex-situ* Multinuclear MAS NMR, *in-situ* NMR and Solutions NMR**
- **Powerful tool to study surface and bulk, structure and chemistry, kinetics and thermodynamics.**

In-Depth Silicon Particle Characterization



Binder Stability

Mixing of Li_7Si_3 with common binder PVDF results in a significant loss of the 7/3 phase.



Also See ES333

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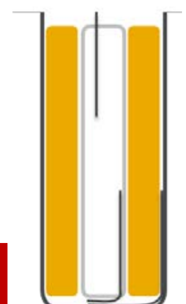
EVALUATION OF SAFETY AND ABUSE TOLERANCE OF SILICON ELECTRODES

Accelerating Rate Calorimetry (ARC) on 18650 Cells

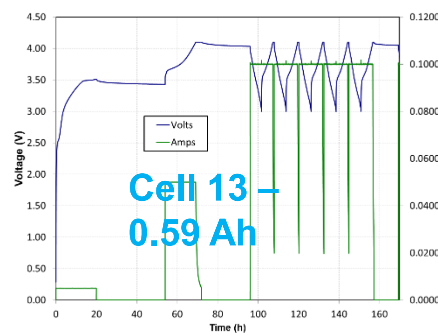
Complete rupture for entire ARC system seen with nano silicon electrodes at both 10 and 15% Si (both ARCs same result) – only a few instances of this occurring in SNL abuse testing

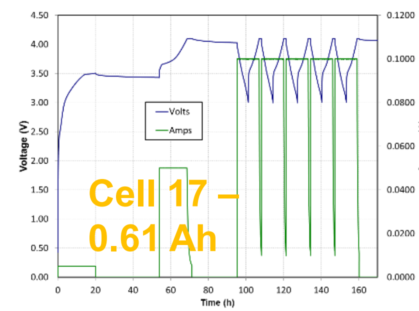
Electrochemical Formation Comparison Between ARC Cells Shows Minimal Variability in Lower Capacity Cells

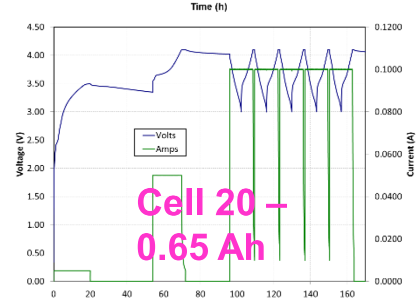
Extra volume occupied by either extra Copper winding or solid copper piece. ~0.6 Ah vs. 1.25 Ah

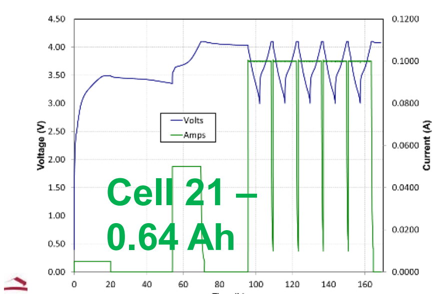


13 and 17 are wound copper
20 and 21 are copper sleeve









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NREL NATIONAL RENEWABLE ENERGY LABORATORY

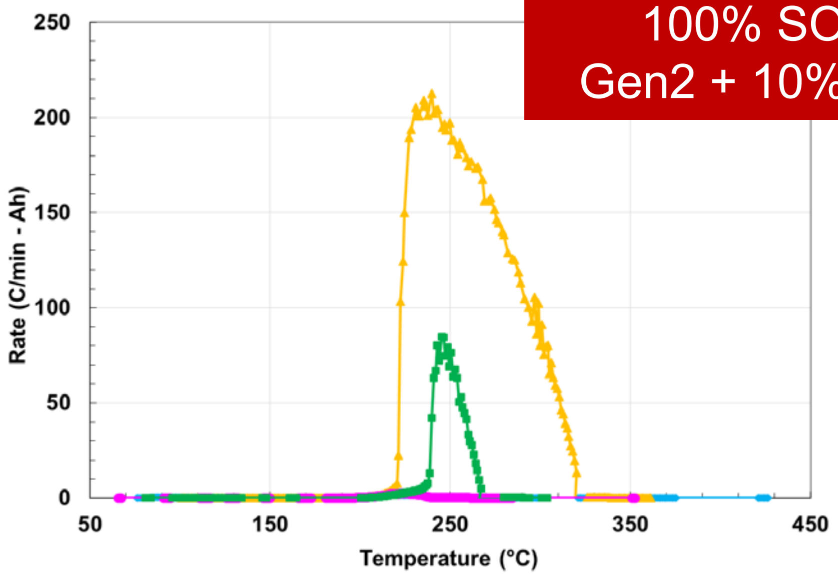
BERKELEY LAB

Argonne NATIONAL LABORATORY

ARC TESTING AND GAS GENERATION DURING ABUSE OF BASELINE NMC532/Si-GR CELLS

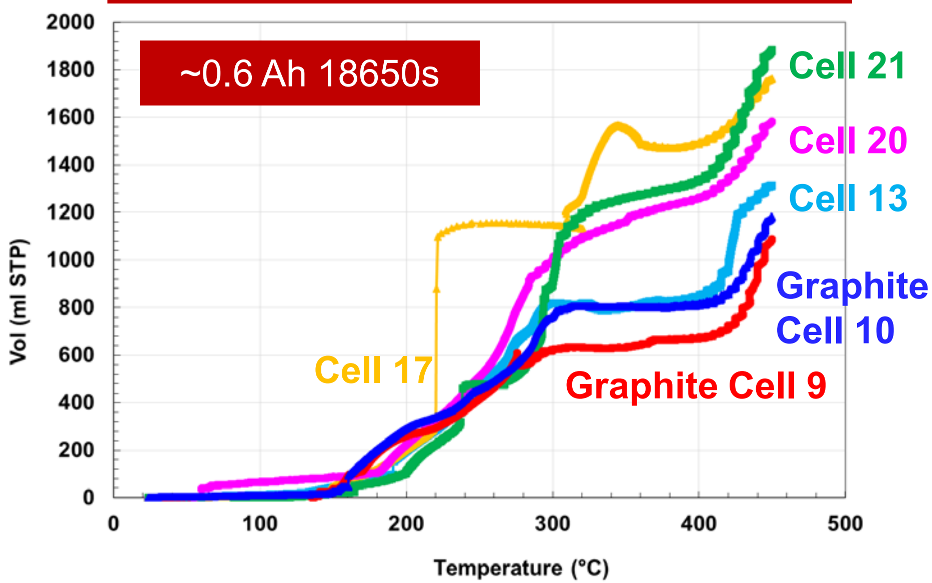
Varies substantially between cells but in all cases higher than similar graphite only 18650s

50-70nm Nanoamor anodes
46 % coating porosity
15% nSi
78% MAG-E
2 % Timcal C45
10 % LiPAA



Four 15% silicon 18650s have been subjected to ARC with wide variability in performance

Observation of intermittent and rapid gas generation during runaway



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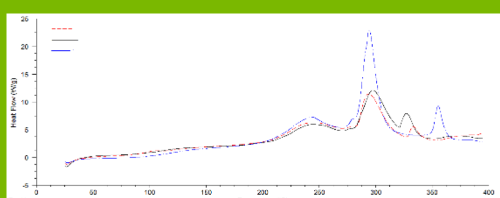
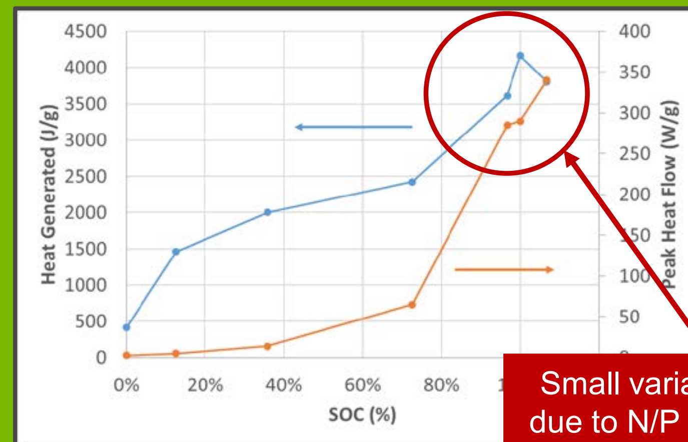
DETERMINING MAJOR CONTRIBUTORS TO RUNAWAY IN SILICON ANODES

2032 Coin Cell Evaluations with Differential Scanning Calorimetry (DSC) Analysis

Significant increase in heat generation for nano scale

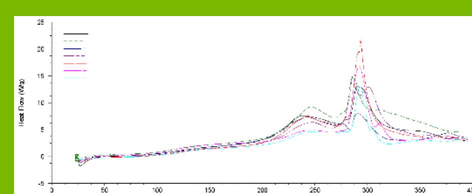
Particle Size	Heat Generation (J/g)	Peak Heat Flow (W/g)
1-5 µm	1364	11.4
500 nm	1430	12.1
70-130 nm	2377	23.0

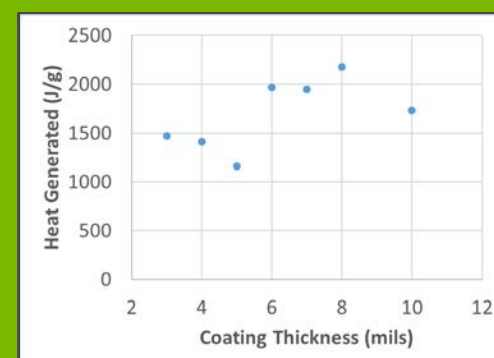




Small variations in SOC due to N/P ratios result in small DSC response

Weak correlation between coating thickness and DSC performance

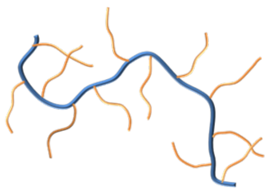


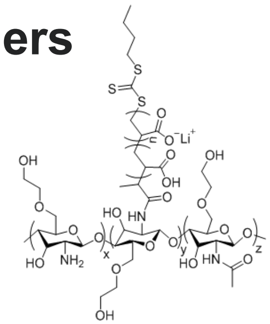


NEXT GENERATION ANODES FOR LITHIUM-ION BATTERIES: MATERIALS ADVANCEMENTS

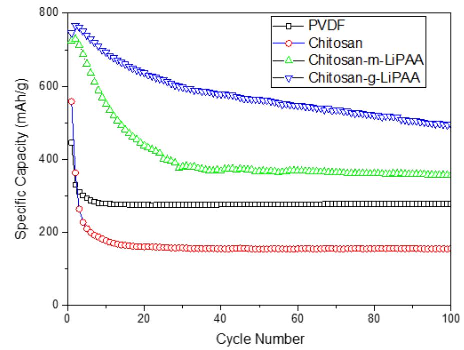
See ES335

- Interfacial Modifications: Additives and Coatings
- Polymer Binders

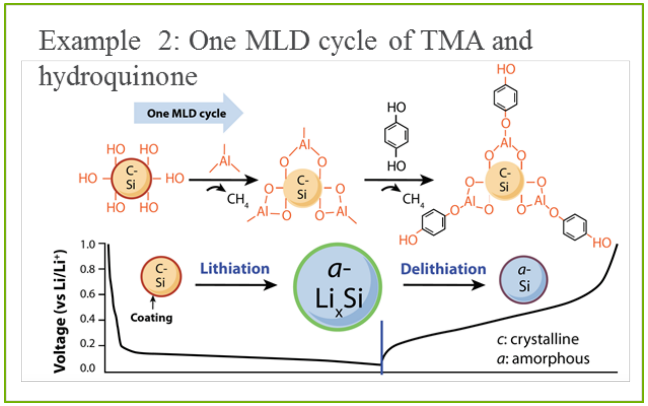




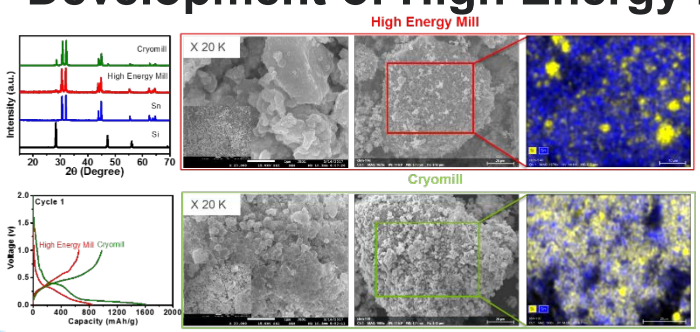
Chitosan-*g*-LiPAA

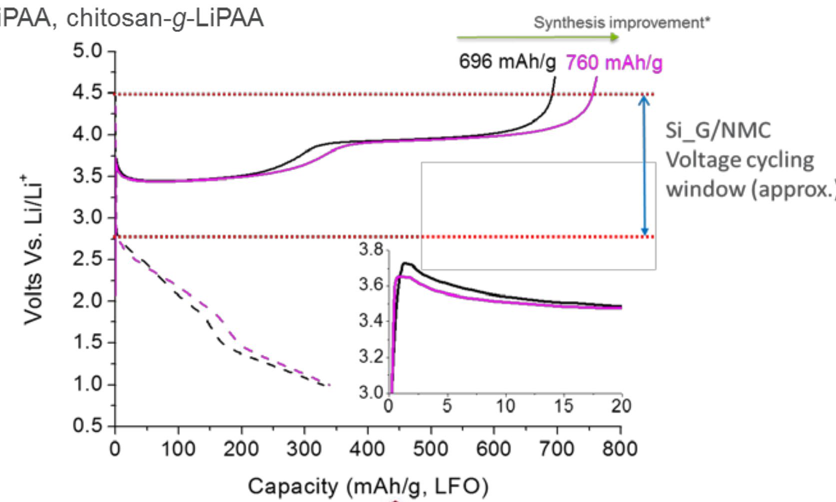


Comparative cycling performance of PVDF, chitosan, chitosan-*m*-LiPAA, chitosan-*g*-LiPAA



- Active Material Development
  - Exploring Li Inventory Strategies
  - Development of High Energy Metals





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REMAINING CHALLENGES AND BARRIERS

- Several key challenges remain that limit integration of silicon into graphitic negative electrodes, mostly related to the large crystallographic expansion of silicon (>300%) upon lithiation.
  - Particle cracking, particle isolation, and electrode delamination.
  - SEI stability issues, which affect cycling efficiency.

RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- We thank the reviewers for their comments, most of which were positive.
  - "outstanding effort to systematically assess advanced anode systems"
  - "preliminary work on program structure, material standards and protocol standards appears to be moving along well"
  - "a good use of resources/synergies of the national laboratories"
- One reviewer pointed out the importance of building in flexibility into this program, which we totally agree and have experienced.
  - "the resource structure may have to change over time with new understanding"
- We apologize that we were not more clear concerning our openness to industrial participation, but that all participation must be open to the whole community.
  - "collaboration is currently with internal contributors, and the reviewer was unclear if industrial partners are sought after or anticipated"

FUTURE WORK

Future Efforts Focused on Building on Accomplishments towards Insights into and Advancement of Diagnostic Studies and Materials and Electrode Development

- Explore and study available materials and promising program materials to integrate into improved baseline materials and electrodes.
- Minimize materials interactions and optimize electrode processing.
- Continue insights through electrochemical and analytical diagnostic studies and explore promising new techniques.
- Maintain close communication and interaction with the Silicon Electrolyte Interface Stabilization (SEI-Sta) Focus Group, building on thier discoveries (see ES333).
- Further evaluation of safety and abuse tolerance of silicon-based cells, focusing on understanding the link between materials properties and abuse response.
- Continue materials development efforts, focusing on promising candidates in full cells (see ES335).

Any proposed future work is subject to change based on funding levels.

SUMMARY

A Wide Range of Insights and Advancements were Attained.

- Explored available silicon materials, as well as material and electrode processing, for improved baseline materials and electrodes. Sample highlights:
  - Identified promising candidate materials.
  - Quantified silicon reactions during aqueous-based processing.
- Extensive electrochemical and analytical diagnostic studies conducted. Sample highlights:
  - Reference electrode studies indicate Impedance rise on cycling is mainly at the positive electrode.
  - Capacity loss is lower for calendar-life than for cycle-life in aged cells.
  - Raman mapping of cycled electrodes shows some silicon is electrochemically inactive
  - NMR and FTIR indicate significant silicon-binder interactions.
  - Prelithiation significantly enhances cycle life
- Conducted calorimetry and abuse tests to determine cell level response. Materials level thermal analysis initiated.
- Materials advancements detailed in separate poster (see ES).

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Berkeley Lab

Argonne NATIONAL LABORATORY

CONTRIBUTORS AND ACKNOWLEDGMENT

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- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)

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